STUDIES OF SILYLATION AGENTS AS THERMAL-OXIDATIVE JET FUEL ADDITIVES

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INTRODUCTION

Derivatization techniques are well known methods to alter species structures to make them more amenable to chemical analysis. Silylation is one type of derivatization process, in which species which contain reactive hydrogen atoms are reacted with an appropriate agent resulting in the conversion of these reactive hydrogen sites to relatively unreactive trimethyl silyl sites (1). Silylation is widely practiced in chromatographic analysis to improve analytical quantitation and transport, increase detectability, increase volatility, and decrease surface interactions. In general, silylating agents are able to react with the active hydrogens in the following species: acids, alcohols, thiols, amines, amides, and enolizable ketones and aldehydes. A variety of agents are known, which vary in their reactivity, selectivity, side reactions, and character of reaction by-products.

Jet fuel is used as a coolant in advanced military aircraft; the hot fuel reacts with dissolved oxygen forming oxidized products. These oxidized products include gums and solid deposits which can coat fuel system surfaces resulting in filter plugging, fouling of close tolerance valves, valve hysteresis, and other problems. Various chemical additives and additive combinations have been utilized to inhibit oxidation and/or reduce deposition. For example the U.S. Air Force JP-8+100 additive package contains a dispersant, an antioxidant, and a metal deactivator. It is generally agreed that the advanced military aircraft being presently conceived will have significantly higher heat loads which will be dumped into the fuel. This higher fuel temperature will result in substantially increased oxygen consumption and subsequent increased deposition.

The substantially higher fuel system temperatures of advanced aircraft will result in complete or near complete oxygen consumption. Additives which delay oxidation, such as antioxidants, metal deactivators, and hydroperoxide decomposers, will be unable to provide significant benefits in reducing deposition under time/temperature conditions where dissolved oxygen consumption is assured. Thus alternative additive techniques need to be explored. Dispersant additives can still be useful under these conditions.

In this study we explore the use of silylation agents as jet fuel additives for reducing oxidative deposition. Silylation agents have the ability to react with the heteroatomic species, such as phenols, which have been implicated in deposit producing mechanisms. Thus they have the potential to chemically transform these species into relatively innocuous silylated products. In this work we study the effect that silylation agents have on jet fuel oxidation and deposition. We show that these additives result in an increased oxidation rate and substantially reduced deposition. These results show that silylation agents may be useful as jet fuel additives for preventing oxidative deposition in advanced aircraft fuel systems including endothermic fuel systems. Silylation agents may also prove to be useful in easing identification of fuel components, particularly those detrimental to fuel thermal stability.

EXPERIMENTAL

Fuel oxidation and deposition characteristics were evaluated in the quartz crystal microbalance/Parr bomb system (QCM) which has been described in detail previously (2,3). All fuel oxidation tests were run at 140C and one atmosphere of air initial pressure. It is heated with a clamp-on band heater and its temperature is controlled by a PID controller through a thermocouple immersed in the fuel. The reactor contains an rf feedthrough, through which the connection for the quartz crystal resonator is attached. The crystals are 2.54 cm in diameter, 0.33 mm thick and have a nominal resonant frequency of 5 MHz. The crystals were acquired from Maxtek Inc. and are available in crystal electrode surfaces of gold, silver, platinum, and aluminum. For the studies reported here gold crystal electrodes were used. The QCM measures deposition (i.e., an increase in mass) which occurs on overlapping sections of the two sided electrodes. Thus, the device responds to deposition which occurs on the metal surface and does not respond to deposition on the exposed quartz.

The device is also equipped with a pressure transducer (Sensotec) to measure the absolute headspace pressure and a polarographic oxygen sensor (Ingold) to measure the headspace oxygen concentration. Previous studies have demonstrated the value of determining the oxidation characteristics of fuels and fuels with additives. A personal computer is used to acquire data at one minute intervals during the experimental run. The following data are recorded during a run: temperature, crystal frequency, headspace pressure, headspace oxygen concentration, and crystal damping voltage.

The reactor is charged with 60 mL of fuel, which is sparged with the appropriate gas for one hour before each test. The reactor is then sealed and the heater is started. All runs in this study were performed at 140C; heat-up time to this temperature is 40±5 minutes. Most runs are conducted for 15 hours, after which the heater is turned off and the reactor allowed to cool. Surface mass measurements can only be determined during the constant temperature (±0.2C) portion of an experimental run. The crystal frequency is converted to a surface mass measurement using the process described below.

The theory that relates the measured frequency changes to surface mass has been presented in detail elsewhere (4). The frequency change of a crystal immersed in a liquid fuel can be due to two effects: the first results from changes in the surface mass density, the second is due to changes in the liquid density and viscosity. At constant temperature and relatively small extents of chemical conversion the liquid properties remain constant and the frequency change can be related to surface deposition via the equation

$$\rho_s = -\left(2.21 \times 10^5 \ g/(cm^2 s)\right)\frac{\Delta f}{f_0^2} \qquad (1)$$

where f_0 is the unperturbed resonant frequency, Δf is the change in resonant frequency, and ρ_s is the surface mass density (mass/area). The reproducibility of the mass deposition measurements on fuels is limited to ±20% for the QCM technique. The fuels studied and some of their properties are listed in Table 1. The fuels were acquired from the Fuels and Lubricants Division of Wright Laboratory, Wright-Patterson AFB, OH, and are referred to by the Wright Lab assigned accession number. Silylation agents were acquired from Pierce Chemical.

The fuels were tested at 140C for 15 hours in a static reactor which utilizes a quartz crystal microbalance (QCM) for measuring deposition, and a polarographic oxygen sensor which monitors the oxygen concentration in the reactor headspace, for monitoring the oxidation process. The experimental apparatus has been described in detail previously (2).

RESULTS AND DISCUSSION

Jet fuel is a complex mixture which is primarily composed of branched and straight chain alkanes, cycloalkanes, and alkyl-substituted aromatics. In addition, various heteroatomic species may be present at relatively small concentrations, including but not limited to: phenols, peroxides, alcohols, organic acids, sulfides, thiols, thiophenes, and amines. In the absence of these heteroatomic species, this hydrocarbon mixture oxidizes readily at elevated temperature via the classic hydrocarbon autoxidation mechanism. For example, a pure alkane, such as dodecane, or a highly treated petroleum fraction, such as Exxsol D-110, will completely consume all available oxygen in the QCM system on the order of minutes at 140C. But, real jet fuels oxidize much more slowly. Even severely hydrotreated fuels require two to five hours to consume the available oxygen at this temperature. Less severely processed fuels can require 5 to 60 hours to consume the available oxygen. These real fuels oxidize more slowly than pure hydrocarbons, due to the presence of these heteroatomic species. These species slow oxidation by intercepting alkyl peroxy radicals and/or by decomposing alkyl hydroperoxides to non-radical products (3,4). Thus the removal of such species should result in a significant increase in the oxidation of the fuel. This effect is illustrated in the hydrotreatment process, which removes heteroatomic species and results in highly oxidizable fuel. These same species which slow oxidation of fuel, also play important roles in forming surface and bulk deposits upon fuel oxidation. Thus, a fuel which is treated to remove such heteroatomic species will oxidize rapidly and display reduced deposition formation.

Treating jet fuel with silylating agents results in the reaction of species with active hydrogens to form trimethylsilyl derivatives. For the case of an alkyl phenol, the following reaction occurs:

We are converting a phenol with a reactive hydrogen to its trimethylsilyl derivative, which is much less reactive and does not contain an active hydrogen. The resulting compound is not reactive towards alkylperoxy radicals (relative to the original phenol) and thus does not interfere with the fuel autoxidation chain. Analogous reactions to the above are also possible for other compounds with active hydrogens.

To explore the effect that silylation has on jet fuel we added one mL of hexamethyldisilazane (HMDS) to 60 mL of fuel F-3119 and stressed this additized fuel in the QCM at 140C for 15 hours. The resulting oxygen sensor and QCM deposition plots for the neat and additized fuel are shown in Figure 1 and 2. The headspace oxygen plot shows that HMDS causes a substantial increase in the oxidation rate of the fuel. The resulting oxygen decay is nearly as fast as a pure hydrocarbon solvent (oxidation complete in 2 to 2.5 hours). The deposition plot shows that HMDS causes a >90% decrease in deposition during the run. It is apparent that treatment of this fuel with HMDS results in significant removal of species which delay oxidation. In addition, removal of these species results in reduced deposition.

It is interesting to compare these results with another technique which removes heteroatomic species, solid-phase extraction (SPE). Of the heteroatomic species present, silica gel SPE removes only those that have significant polarity. Previously, we have demonstrated that SPE treatment reduces deposition significantly, but does not increase oxidation as substantially (2).

To investigate the chemical changes that occur in the fuel upon silylation treatment we used gas chromatography–mass spectrometry (GC-MS) after preconcentration of the polar fuel species via SPE with subsequent methanol back extraction. This technique is particularly useful for identification of phenol species in the fuel. The results of these analyses (not shown) demonstrate substantial conversion of fuel phenols to their silylated derivatives.

There exist a variety of silylation reagents which display varying silylation selectivity, reactivity, side reactions, and character of reaction by-products. For example, while HMDS requires elevated temperatures for reaction, silylation with N,O-bis[trimethyl]acetamide (BSA) can be performed at room temperature. We therefore have the ability to control the time and/or temperature at which the silylation reaction occurs. The ability to remove phenols within aircraft fuel lines during the heating of the fuel in its transport through the fuel system is highly desirable. The presence of phenols can be desirable during fuel storage as they inhibit oxidation, but their presence is undesirable in fuel systems due to their contribution to fouling. By proper choice of a silylation additive, we may be able to design a fuel where the silylation reaction occurs at a location of choice in the fuel system with subsequent rapid consumption of oxygen.

The promise of silylation additives does not come without potential disadvantages. These include cost, water sensitivity, and problems due to product formation in combustors. Presently, silylation additives are relatively expensive, when compared to common jet fuel additives, as they are produced in relatively small quantities for derivatization in chemical analysis. Silylation reagents react rapidly with water and humid air forming undesirable silanols. It is expected that silylating reagents and silylated products will be rapidly oxidized to silicon dioxide within the combustion chamber. This may have a negative effect on combustor and turbine materials depending on the physical form of the silicon dioxide product.

CONCLUSIONS

In this study we explore the use of silylation agents as jet fuel additives for reducing oxidative deposition. Silylation agents have the ability to react with the heteroatomic species, such as phenols, which have been implicated in deposit producing mechanisms. Thus they have the potential to chemically transform these species into relatively innocuous silylated products. In this work we study the effect that silylation agents have on jet fuel oxidation and deposition. We show

that these additives result in an increased oxidation rate and substantially reduced deposition. These results show that silylation agents may be useful as jet fuel additives for preventing oxidative deposition in advanced aircraft fuel systems including endothermic fuel systems. Silylation agents may also prove to be useful in easing identification of fuel components, particularly those detrimental to fuel thermal stability.

ACKNOWLEDGMENTS

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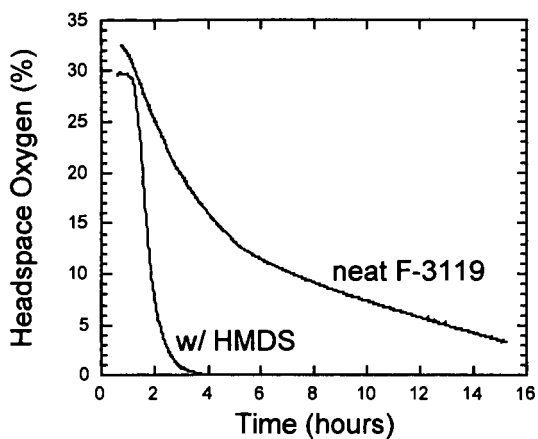
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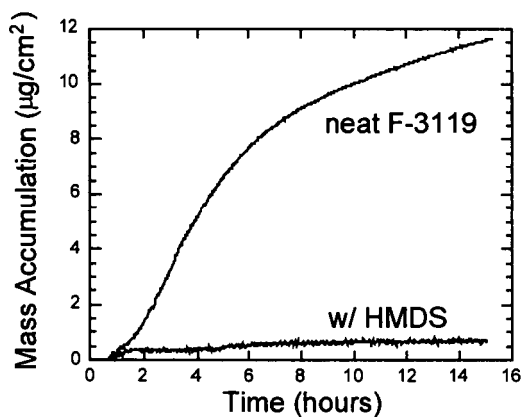**Figure 1. Plots of Headspace Oxygen for Fuel F-3119 with and without HMDS.**

Figure 2. Plots of Mass Accumulation for Fuel F-3119 with and without HMDS.